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(54) CURABLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a curable composition which has excellent heat resistance and weather resistance, and further to provide a curable composition having excellent curability.

SOLUTION: This curable composition comprises (I) a vinyl polymer having at least one cross-linkable functional group and (II) an antioxidant. The curable composition having improved curability, wherein a vinyl polymer having cross-linkable functional silyl groups represented by general formula (1): SiY_aR_3-a (1) [R is a 1 to 20C alkyl or the like; Y is OH or a hydrolysable group; (a) is 1, 2 or 3, especially 3] is used.

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CLAIMS

[Claim (a)]

[Claim 1] The following two components: The vinyl system polymer (I) which has at least one cross-linking functional group, and the hardenability constituent containing an antioxidant (III).
[Claim 2] The hardenability constituent according to claim 1 characterized by containing the vinyl system polymer (I) whose molecular weight distribution is less than 1.8.
[Claim 3] The hardenability constituent according to claim 1 or 2 characterized by containing the vinyl system polymer (I) which is what is manufactured by mainly carrying out the polymerization of the monomer chosen from the group which a principal chain becomes from an acrylic (meta) monomer, an acrylonitrile system monomer, an aromatic series vinyl system monomer, a fluorine content vinyl system monomer, and a silicon content vinyl system monomer.
[Claim 4] The hardenability constituent according to claim 3 characterized by a principal chain containing the vinyl system polymer (I) which is an acrylic (meta) polymer.
[Claim 5] The hardenability constituent according to claim 4 characterized by a principal chain containing the vinyl system polymer (I) which is an acrylic polymer.
[Claim 6] The hardenability constituent according to claim 5 characterized by a principal chain containing the vinyl system polymer (I) which is an acrylic ester system polymer.
[Claim 7] It is a hardenability constituent given in any 1 term among claims 1-6 to which the cross-linking functional group of a vinyl system polymer (I) is characterized by being a cross-linking silyl radical.
[Claim 8] It is a hardenability constituent given in any 1 term among claims 1-6 to which the cross-linking functional group of a vinyl system polymer (I) is characterized by being an alkynyl radical.
[Claim 9] It is a hardenability constituent given in any 1 term among claims 1-6 to which the cross-linking functional group of a vinyl system polymer (I) is characterized by being a hydroxyl group.
[Claim 10] It is a hardenability constituent given in any 1 term among claims 1-6 to which the cross-linking functional group of a vinyl system polymer (I) is characterized by being an amino group.
[Claim 11] A hardenability constituent given in any 1 term of claims 1-6 characterized by the cross-linking functional group of a vinyl system polymer (I) being a radical which has the carbon-carbon double bond of polymerization nature.
[Claim 12] It is a hardenability constituent given in either among claims 1-6 to which the cross-linking functional group of a vinyl system polymer (I) is characterized by being an epoxy group.
[Claim 13] It is a hardenability constituent given in any 1 term among claims 1-12 characterized by containing the vinyl system polymer whose principal chain is what is manufactured by the living radical polymerization method.
[Claim 14] The hardenability constituent according to claim 13 characterized by a living radical polymerization containing the vinyl system polymer which is an atomic migration radical polymerization.
[Claim 15] The hardenability constituent according to claim 14 with which an atomic migration radical polymerization is characterized by containing the vinyl system polymer with which the

complex chosen from the transition metal complex which uses the 7th group of the periodic table, eight groups, nine groups, ten groups, or 11 group element as a central metal is made into a catalyst.

[Claim 16] The hardenability constituent according to claim 15 characterized by containing the vinyl system polymer which is a complex with which the metal complex made into a catalyst is chosen from the group which it becomes from the complex of copper, nickel, a ruthenium, or iron.
[Claim 17] The hardenability constituent according to claim 16 characterized by containing the vinyl system polymer whose metal complex made into a catalyst is a copper complex.
[Claim 18] It is a hardenability constituent given in any 1 term among claims 1-17 characterized by containing the vinyl system polymer which is the cross-linking silyl radical whose α is 3 among the cross-linking silyl radicals as which a cross-linking functional group is expressed in a general formula (1), and hardenability improving.
$$-SiR_3R'_3-\alpha-(1)$$

however, the inside R of a formula — the alkyl group of carbon numbers 1-20, and the aryl group of carbon numbers 6-20 — The aralkyl radical or (R') $3SiO$ of carbon numbers 7-20 — (R' is the univalent hydrocarbon group of carbon numbers 1-20) three R' — being the same — differing — — — — when the Tori ORGANO siloxy radical shown is shown and two or more R exists, they may be the same and may differ. When Y shows a hydroxyl group or a hydrolysis nature machine and two or more Y exists, they may be the same and may differ. α shows 1, 2, or 3.
[Claim 19] The hardenability constituent according to claim 18 characterized by containing the vinyl system polymer which has a cross-linking silyl radical at the principal chain end.
[Claim 20] It is a hardenability constituent given in any 1 term among claims 1-19 characterized by containing the vinyl system polymer with which a vinyl system polymer contains only the cross-linking silyl radical whose α is 3 among the cross-linking silyl radicals expressed with a general formula (1).
[Claim 21] It is a hardenability constituent given in any 1 term among claims 1-20 characterized by containing the vinyl system polymer which is a polymer with which some or all of a vinyl system polymer has simultaneously the cross-linking silyl radical whose α is 1 or 2 among the cross-linking silyl radical whose α is 3 among the cross-linking silyl radicals expressed with a general formula (1), and the cross-linking silyl radical expressed with a general formula (1).
[Claim 22] It is a hardenability constituent given in any 1 term among claims 1-20 characterized by a vinyl system polymer containing the vinyl system polymer of both the polymer which has the cross-linking silyl radical whose α is 3 among the cross-linking silyl radicals expressed with a general formula (1), and the polymer which has the cross-linking silyl radical whose α is 1 or 2 among the cross-linking silyl radicals expressed with a general formula (1).
[Claim 23] It is a hardenability constituent given in any 1 term among claims 1-20 characterized by a vinyl system polymer containing the vinyl system polymer of both the polymer which has the cross-linking silyl radical whose α is 3 among the cross-linking silyl radicals expressed with a general formula (1), and the polymer which has only the cross-linking silyl radical whose α is 1 or 2 among the cross-linking silyl radicals expressed with a general formula (1).
[Claim 24] It is a hardenability constituent given in any 1 term among claims 1-20 characterized by a vinyl system polymer containing only the vinyl system polymer which has only the cross-linking silyl radical whose α is 3 among the cross-linking silyl radicals expressed with a general formula (1).
[Claim 25] The vinyl system polymer with which a vinyl system polymer has only the cross-linking silyl radical whose α is 3 among the cross-linking silyl radicals expressed with a general formula (1). And the vinyl system polymer of both vinyl system polymers which are polymers which have simultaneously both cross-linking silyl radicals whose α is 1 or 2 among the cross-linking silyl radicals expressed with the cross-linking silyl radical and general formula (1) whose α is 3 among the cross-linking silyl radicals expressed with a general formula (1) It is a hardenability constituent given in any 1 term among claims 1-20 characterized by containing.
[Claim 26] It is a hardenability constituent given in any 1 term among claims 1-20 characterized by a vinyl system polymer containing the vinyl system polymer of both the polymer which has

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only the cross-linking silyl radical whose α is 3 among the cross-linking silyl radicals expressed with a general formula (1), and the polymer which has the cross-linking silyl radical whose α is 1 or 2 among the cross-linking silyl radicals expressed with a general formula (1).
[Claim 27] It is a hardenability constituent given in any 1 term among claims 1-20 characterized by a vinyl system polymer containing the vinyl system polymer of both the polymer which has only the cross-linking silyl radical whose α is 3 among the cross-linking silyl radicals expressed with a general formula (1), and the polymer which has only the cross-linking silyl radical whose α is 1 or 2 among the cross-linking silyl radicals expressed with a general formula (1).
[Claim 28] It is a hardenability constituent given in any 1 term among claims 1-27 to which an antioxidant (II) is characterized by being an antioxidant (III).
[Claim 29] It is a hardenability constituent given in any 1 term among claims 1-28 to which an antioxidant (III) is characterized by being a hindered phenol system.
[Claim 30] It is a hardenability constituent given in any 1 term among claims 1-29 characterized by adding light stabilizer (IV) further.
[Claim 31] It is a hardenability constituent given in any 1 term among claims 1-30 characterized by light stabilizer (IV) being a kind or two sorts or more of things chosen from the group which consists of a hindered amine light stabilizer, benzoate system light stabilizer, benzotriazol system light stabilizer, and benzophenone system light stabilizer.
[Claim 32] It is a hardenability constituent given in any 1 term among claims 1-27 to which an antioxidant (II) is characterized by being light stabilizer (IV').
[Claim 33] It is [claims 1-27 to which light stabilizer (IV') is characterized by being an ultraviolet ray absorbent, or] a hardenability constituent given in any 1 term among 32.
[Claim 34] It is [claims 1-27 characterized by light stabilizer (IV') being a kind or two sorts or more of things chosen from the group which consists of a hindered amine light stabilizer, benzoate system light stabilizer, benzotriazol system light stabilizer, and benzophenone system light stabilizer, or] a hardenability constituent given in any 1 term among 32 and 33.
[Claim 35] It is [claims 1-27 characterized by combining an ultraviolet ray absorbent and a hindered amine system as light stabilizer (IV), or] a hardenability constituent given in any 1 term among 32-34.
[Claim 36] It is [claims 1-27 characterized by adding an antioxidant (III) further, or] a hardenability constituent given in any 1 term among 32-35.
[Claim 37] It is [claims 1-27 to which an antioxidant (III) is characterized by being a hindered phenol system, or] a hardenability constituent given in any 1 term among 32-36.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a hardenability constituent. Furthermore, the vinyl system polymer which has in detail the cross-linking silyl radical whose a is 3 while the vinyl system polymer (I) which has following at least one 2 component: cross-linking functional group, the thing about the hardenability constituent containing an antioxidant (II), and a cross-linking functional group are cross-linking silyl radicals expressed with a general formula (I) is contained, and it is related with the hardenability constituent whose hardenability improved.

- SiYR3-a ... (I)

(However, it is the same as the above the inside Y, R, and a of a formula.)

[0002]

[Description of the Prior Art] What has a functional group at a functional group, especially the end with the polymer of the vinyl system obtained by the radical polymerization by one side of the polymer obtained by ionic polymerization or condensation polymerization is hardly put in practical use yet. What the acrylic (meta) polymer has the property which is not acquired in the above-mentioned polyether system polymers, such as high weatherability and transparency, a hydrocarbon system polymer, or a polyester system polymer, and has an alkenyl radical and a cross-linking silyl radical in a side chain also in a vinyl system polymer is used for the coating of high weatherability etc. On the other hand, polymerization control of an acrylic polymer is not easy because of the side reaction, and installation of the functional group to an end etc. is dramatically difficult.

[0003] If the vinyl system polymer which has an alkenyl radical at the chain end can be obtained by the simple approach, the hardened material which excelled [side chain] in hardened material physical properties as compared with what has a cross-linking radical can be obtained.

Therefore, although the manufacturing method has been examined by the researcher of the former many, it is not easy to manufacture them industrially. For example, the synthesis method of the acrylic polymer which has an alkenyl radical at the end (meta) which uses alkenyl radical content disulfide as a chain transfer agent is indicated by JP.1-247403.A and JP.5-255415.A.

[0004] In JP.5-262808.A, the vinyl system polymer which has hydroxyl in both ends is compounded using the disulfide which has hydroxyl, and the synthesis method of the acrylic polymer which has an alkenyl radical at the end (meta) is further indicated using the reactivity of hydroxyl.

[0005] In JP.5-211922.A, the vinyl system polymer which has hydroxyl in both ends is compounded using the polysulfide which has hydroxyl, and the synthesis method of the acrylic polymer which has a silyl radical at the end (meta) is further indicated using the reactivity of hydroxyl.

[0006] By these approaches, it is difficult to introduce a functional group into both ends certainly, and the hardened material which has a satisfactory property cannot be obtained. In order to introduce a functional group into both ends certainly, a chain transfer agent must be used for a large quantity, and it is a production process too problem. Moreover, since the usual radical polymerization is used by these approaches, the molecular weight of the polymer obtained

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2006/10/12

and control of molecular weight distribution (ratio of weight average molecular weight and number average molecular weight) are difficult.

[0007] Artificers have invented many to such a Prior art about the vinyl system polymer which has cross-linking functional groups various until now at the end, its manufacturing method, a hardenability constituent, and an application (see JP.11-080249.A, JP.11-080250.A, JP.11-005815.A, JP.11-116817.A, JP.11-116808.A, JP.11-080571.A, JP.11-080570.A, JP.11-130931.A, JP.11-100433.A, JP.11-116783.A, JP.9-272714.A, JP.9-272715.A, etc.).

[0008] For example, the silicon content radical which can construct a bridge by having the hydroxyl group or hydrolysis nature machine combined with the silicon atom, and forming siloxane association. The hardened material obtained from the vinyl system polymer which has (it is also hereafter called a "cross-linking silyl radical"), or its constituent. The sealing material in a structural elastic sealing compound sealant, the sealing material for multiple glass, etc. although it excels in thermal resistance or weatherability and especially definition is not carried out. Electrical insulation materials, such as electrical and electric equipment and electronic-parts ingredients, such as a solar-battery rear-face sealing agent, and pre-insulation an electric wire, material for cables, A binder, adhesives, elastic adhesives, a coating, powder coatings, a coating material, foam, Sealants, such as a can top, the potting agent for electric electronics, a film, a gasket, it is available for various applications, such as seals, such as a fluid-sealant agent used in a casting ingredient, various molding materials, an artificial marble and wired glass, and rust proofing and the sealing agent for water proof of a glass laminate end face (cutting section), autopaets, electrical machinery components, various machine parts, etc.

[0009]

[Problem(s) to be Solved by the Invention] However, even if it uses such a vinyl system polymer that is generally excellent in weatherability or thermal resistance, under a severe condition, it cannot bear further. For example, it is the case where it will be used in the strong location of ultraviolet rays, such as up [of snow and ice], for a long period of time for 10,000 years etc. also in the case where it is used for the circumference of the engine of an automobile, the seal near the heat source, etc. for a long period of time, etc. the district where the LAT is low, or high ground.

[0010] Moreover, the polymer which has the hydrolysis nature silicon radical with which two adding-water nature resolvability radicals per silicon atom come to combine the vinyl system polymer which has such a cross-linking silyl radical was used in many cases.

[0011] When having used it at the application etc. and low temperature of adhesives and you needed a very quick cure rate especially, the cure rate was not enough, and crosslinking density needed to be reduced, therefore since crosslinking density was not enough, there was a problem that there was stickiness (surface tack) to take out the flexibility after hardening. Then, this invention aims at offering the hardenability constituent which is excellent in thermal resistance, weatherability, and hardenability.

[0012]

[Means for Solving the Problem] The vinyl system polymer which has at least one cross-linking functional group as a result of examining this invention wholeheartedly in view of the above-mentioned actual condition (I). That the above-mentioned technical problem is improvable by using the hardenability constituent containing an antioxidant (II) And a header. Moreover, a header and this invention were reached [that hardenability is further improvable and] by using the hardenability constituent containing the vinyl system polymer which has the cross-linking silyl radical whose a is 3 among the cross-linking silyl radicals expressed with a general formula (I).

- SiYR3-a ... (I)

(However, it is the same as the above the inside Y, R, and a of a formula.)

Although especially the principal chain of a vinyl system polymer is not limited, an acrylic (meta) monomer, it is desirable to mainly carry out the polymerization of the monomer chosen from the group which consists of an acrylonitrile system monomer, an aromatic series vinyl system monomer, a fluorine content vinyl system monomer, and a silicon content vinyl system monomer, and to be manufactured. more — desirable — an acrylic (meta) monomer — further — desirable

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2006/10/12

— an acrylic monomer — it is more preferably desirable an acrylic ester system monomer and to carry out a polymerization and to be most preferably, manufactured using a butyl acrylate system monomer.

[0013] Although especially a vinyl system polymer is not limited, it is desirable that the value of the ratio (Mw/Mn) of the weight average molecular weight (Mw) measured with gel permeation chromatography and number average molecular weight (Mn) is less than 1.8.

[0014] Although especially the principal chain of a vinyl system polymer is not limited, being manufactured by the living radical polymerization method is desirable, and it is more desirable to be manufactured by the atomic migration radical polymerization method. In that case, especially as a catalyst of an atomic migration radical polymerization method, although not limited, it is desirable that it is the complex of the metal chosen from the group which consists of copper, nickel, a ruthenium, and iron, and it is more desirable that it is a copper complex.

[0015] The location of the cross-linking silyl radical of a vinyl system polymer has a desirable end, although definition is not carried out. In addition, although you may have the same silyl radical as the interior of a principal chain, when asking for rubber elasticity the hardened material made to construct a bridge, it is desirable to have a silyl radical only at the end.

[0016] Although especially the number of the cross-linking silyl radicals of a vinyl system polymer is not limited, in order to obtain a hardened material with more high cross-linking, it is averaged and is 1.5 or more pieces more preferably 1.2 or more pieces one or more pieces.

[0017] Although definition is not carried out, as for a vinyl system polymer, being manufactured by the living radical polymerization is desirable, and it is more desirable that it is an atomic migration radical polymerization. Furthermore, although definition is not carried out, as for an atomic migration radical polymerization, it is desirable to make into a catalyst the complex chosen from the transition metal complex which uses the 7th group of the periodic table, eight groups, nine groups, ten groups, or 11 group element as a central metal, its complex chosen from the group which consists of a complex of copper, nickel, a ruthenium, or iron is more desirable, and especially a copper complex is desirable [a radical polymerization] especially.

[0018]

[Embodiment of the Invention] This invention relates to a hardenability constituent. Furthermore, in detail, while the vinyl system polymer (I) which has following at least one 2 component: cross-linking functional group, the thing about the hardenability constituent containing an antioxidant (II), and a cross-linking functional group are cross-linking silyl radicals expressed with a general formula (I), a is related with the hardenability constituent containing the vinyl system polymer which has the cross-linking silyl radical which is 3.

- SiYR3-a ... (I)

(However, it is the same as the above the inside Y, R, and a of a formula.)

Below, the hardenability constituent of this invention is explained in full detail.

About << vinyl system polymer, >> [principal chain] artificers The vinyl system polymer which has cross-linking functional groups various until now at the polymer end. The manufacturing method, a hardenability constituent. And it is related with an application. Much invention The line came. JP.11-080249.A, JP.11-080250.A, JP.11-005815.A, JP.11-116817.A, JP.11-116808.A, JP.11-080571.A, JP.11-080570.A, JP.11-130931.A, and JP.11-100433.A — Refer to JP.11-116783.A, JP.9-272714.A, JP.9-272715.A, etc. Although not limited especially as a vinyl system polymer (I) of this invention, all the polymers indicated by invention illustrated above can be used suitably.

[0019] It is not limited especially as a vinyl system monomer which constitutes the principal chain of the vinyl system polymer of this invention, but various kinds of things can be used. If it illustrates, an acrylic acid (meta), a methyl acrylate (meta), An ethyl acrylate, acrylic-acid (meta)-n-propyl, acrylic-acid (meta) isopropyl, (Meta) Acrylic-acid-n-butyl, isobutyl acrylate (meta), (Meta) Acrylic-acid-tert-butyl, acrylic-acid (meta)-n-pentyl, (Meta) Acrylic-acid-n-hexyl, acrylic-acid (meta) cyclohexyl, (Meta) Acrylic-acid-n-heptyl, acrylic-acid (meta)-n-octyl, (Meta) 2-ethylhexyl acrylate, acrylic-acid (meta) nonyl, (Meta) Acrylic-acid DESHIRU, acrylic-acid (meta) dodecyl, acrylic-acid (meta) phenyl, (Meta) Acrylic-acid toluyl, acrylic-acid (meta) benzyl, acrylic-acid (meta)-2-methoxy ethyl, (Meta) Acrylic-acid-3-methoxy butyl, acrylic-acid

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(meta)-2-hydroxyethyl, (Meta) 2-hydroxypropyl acrylate, acrylic-acid (meta) stearyl, (Meta) Metacyclicidyl acrylate, acrylic-acid (meta) 2-aminoethyl, (Meta) gamma-(methacryloyl oxypropyl) trimethoxysilane, the ethyleneoxide addition product of an acrylic acid (meta), Acrylic-acid trifluoromethyl methyl, an acrylic-acid (meta) 2-trifluoro methylethyl, (Meta) Acrylic-acid 2-perfluoro ethyl ethyl, acrylic-acid (meta) 2-perfluoro ethyl-2-perfluoro butyl ethyl, (Meta) Acrylic-acid 2-perfluoro ethyl, acrylic-acid (meta) perfluoro methyl, (Meta) Acrylic-acid JPA fluoro methyl methyl, acrylic-acid (meta) 2-perfluoro methyl-2-perfluoro ethyl methyl, (Meta) Acrylic-acid 2-perfluoro hexyl ethyl, acrylic-acid (meta) 2-perfluoro DESHIRU ethyl, (Meta) Acrylic (meta) monomers, such as acrylic-acid 2-perfluoro hexadecyl ethyl; Styrene, (Meta) Aromatic series vinyl system monomers, such as vinyltoluene, alpha methyl styrene, KURORU styrene, a styrene sulfonic acid, and its salt; Perfluoro ethylene, Fluorine content vinyl system monomers, such as perfluoro propylene and vinylidene fluoride; Vinyltrimethoxysilane, Silicon content vinyl system monomers, such as vinyltriethoxysilane; A maleic anhydride, Monoalkyl ester and dialkyl ester of a maleic acid and a maleic acid; A fumaric acid, Monoalkyl ester and dialkyl ester of a fumaric acid; Maleimide, Methyl maleimide, ethylmaleimide, propyl maleimide, butylmaleimide, Hexyl maleimide, octyl maleimide, dodecyl maleimide, stearyl maleimide, Maleimide system monomers, such as phenyl maleimide and cyclohexyl maleimide; Acrylonitrile, Acrylonitrile system monomers, such as a methacrylonitrile; Acrylamide, Amide group content vinyl system monomers, such as methacrylamide; Vinyl acetate, Conjugated dienes, such as alkenes; butadienes, such as vinyl ester, ethylene, such as propionic-acid vinyl, vinyl pivalate, benzoic-acid vinyl, and cinnamic acid vinyl, and a propylene, and an isoprene; a vinyl chloride, a vinylidene chloride, an allyl chloride, an allyl alcohol, etc. are mentioned. These may be used independently, and even if it carries out copolymerization of the plurality, they are not cared about.

[0020] It is desirable that it is what is manufactured by mainly carrying out the polymerization of at least one monomer chosen from the group which the principal chain of a vinyl system polymer becomes from an acrylic (meta) monomer, an acrylonitrile system monomer, an aromatic series vinyl system monomer, a fluorine content vinyl system monomer, and a silicon content vinyl system monomer. here — "mainly" — it means more than 50 mol % and that it is the above-mentioned monomer 70% or more of preferably among the monomeric units which constitute a vinyl system polymer.

[0021] Especially, the styrene system monomer from physical properties etc. and (meta) acrylic-acid system monomer of a product are desirable. More preferably, it is an acrylic ester monomer and a methacrylic ester monomer, is an acrylic ester monomer especially preferably, and is butyl acrylate still more preferably. In this invention, it is desirable other monomers, copolymerization, and that may carry out block copolymerization further and these desirable monomers are contained 40% by the weight ratio in these desirable monomers in that case. In addition, an acrylic acid (meta) expresses an acrylic acid and/or, or a methacrylic acid with the above-mentioned transcription.

[0022] Although especially the molecular weight distribution of the vinyl system polymer of this invention, i.e., the ratio of the weight average molecular weight (Mw) and number average molecular weight (Mn) which were measured with gel permeation chromatography, (Mw/Mn) are not limited, it is less than 1.8 preferably, is 1.7 or less more preferably, is 1.8 or less still more preferably, is 1.5 or less still more preferably, is 1.4 or less especially preferably, and is 1.3 or less most preferably. In the GPC measurement by this invention, using chloroform as a mobile phase, a polystyrene gel column can perform measurement and number average molecular weight etc. can usually be calculated by polystyrene conversion.

[0023] Although especially a limit does not have the number average molecular weight of the vinyl system polymer in this invention, when it measures with gel permeation chromatography, the range of 500-1,000,000 is desirable, 1,000-100,000 are more desirable, and 5,000-50,000 are still more desirable.

Although definition is not carried out, the synthesis method of the vinyl system polymer in <synthesis method of principal chain> this invention has a desirable control radical polymerization, is more desirable, and is desirable, [of especially an atomic migration radical

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2006/10/12

polymerization) [of a living radical polymerization] These are explained below.

A control radical polymerization radical polymerization method can be classified into "the general radical polymerization method" to which copolymerization of the monomer which has a specific functional group, and the vinyl system monomer is only carried out, and the "control radical polymerization method" which can introduce a specific functional group into the location controlled [end], using an azo system compound, a peroxide, etc. as a polymerization initiator. [0024] Although "a general radical polymerization method" is a simple approach, since the monomer which has a specific functional group by this approach is not introduced into a probable polymer, when it is going to obtain a polymer with the high rate of organic-functions-izing, it is necessary to use this monomer for a large quantity considerably, and there is a trouble that the rate of a polymer that this specific functional group is not introduced into reverse by little activity becomes large. Moreover, since it is a free radical polymerization, the trouble that only a large polymer with high viscosity is obtained also has molecular weight distribution.

[0025] A "control radical polymerization method" can be classified into the "chain transfer agent method" the vinyl system polymer which has a functional group at the end is obtained, and the "living radical polymerization method" the polymer of the molecular weight as a design is mostly obtained by growing without a polymerization growth end causing termination reaction etc., by performing a polymerization using the chain transfer agent which has a further specific functional group.

[0026] Although a "chain transfer agent method" can obtain a polymer with the high rate of organic-functions-izing, the chain transfer agent which has the specific functional group of a large quantity considerably to an initiator is required for it, and it has a problem on the financial side also including processing. Moreover, like the above-mentioned "general radical polymerization method", since it is a free radical polymerization, the trouble that it is large and only a polymer with high viscosity is obtained also has molecular weight distribution.

[0027] While termination reaction cannot occur easily and the narrow (Mw/Mn is 1.1 to about 1.5) polymer of molecular weight distribution is obtained though it is the radical polymerization made difficult [control] since the termination reaction a "living radical polymerization method" has a high rate of polymerization, and according to coupling of radicals etc. tends to occur unlike these polymerization methods, molecular weight is freely controllable with the preparation ratio of a monomer and an initiator.

[0028] Therefore, a "living radical polymerization method" has narrow molecular weight distribution, and is more desirable as the manufacture approach of a vinyl system polymer of having the above-mentioned specific functional group for the monomer which can obtain a polymer with low viscosity upwards and has a specific functional group since [of a polymer] it can introduce into the location of arbitration mostly.

[0029] In addition, although living polymerization means the polymerization to which an end always continues having activity and the chain grows in the narrow sense, the pseudo-living polymerization which grows while that by which the end was inactivated, and the activated thing are generally in an equilibrium state is also contained. The definition in this invention is also the latter.

[0030] As for the "living radical polymerization method", research is positively made into groups various in recent years. As the example, for example A journal OBU American chemical society (J. Am.Chem.Soc.), 1994, 118 volumes, the thing using a cobalt porphyrin complex as shown in 7943 pages, Macro leakage-at-bulb KYURUZU (Macromolecules), 1994, The thing using radical scavengers, such as 27 volumes and a nitroxide compound as shown in 7228 pages, "The atomic migration radical polymerization" (Atom Transfer Radical Polymerization:ATRP) etc. which makes an organic halogenide etc. an initiator and makes a transition metal complex a catalyst is raised.

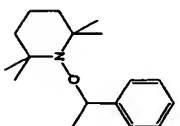
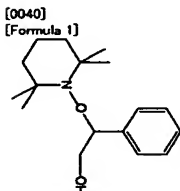
[0031] Also in a "living radical polymerization method", an organic halogenide or a halogenation sulfonyl compound An initiator, "The atomic migration radical polymerization method" which carries out the polymerization of the vinyl system monomer by making a transition metal complex into a catalyst. As the manufacture approach of a vinyl system polymer of in addition to the description of the above-mentioned "living radical polymerization method" having a halogen comparatively advantageous to a functional-group conversion reaction etc. at the end, and

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2006/10/12

JP.2003-113324.A [DETAILED DESCRIPTION]

7/10 ページ



If what has functional groups, such as a hydroxyl group as it shown in the above figure, is used when using an alkoxy amine compound as an initiator, the polymer which has a functional group at the end will be obtained. If this is used for the approach of this invention, the polymer which has a functional group at the end will be obtained.

[0041] Although polymerization conditions, such as the monomer and solvent which are used by the polymerization using radical scavengers, such as the above-mentioned nitroxide compound, and polymerization temperature, are not limited, they are the same as that of what is used about the atomic migration radical polymerization explained below, and are not cared about.

The more desirable atomic migration radical polymerization method as an atomic migration radical polymerization, next a living radical polymerization of this invention is explained.

[0042] In this atomic migration radical polymerization, an organic halogenide especially the organic halogenide (for example, the carbonyl compound which has a halogen in an alpha position and the compound which has a halogen in the benzylic position) which has reactant high carbon-halogen association, or a halogenation sulfonyl compound is used as an initiator. It illustrates concretely — if it becomes — C6H5-CH2X, C6H5-C(H)(X)CH3, and C6H5-C(X)(CH3) — two However, the inside of the upper chemical formula, C6H5 is a phenyl group and X chlorine, a bromine, or iodine —

R1-C(H)(X)-CO two R2, R1-C(CH3)(X)-CO two R2, R1-C(H)(X)-C(O)R2, R1-C(CH3)(X)-C(O)R2 (among a formula). For R1 and R2, a hydrogen atom or the alkyl group of carbon numbers 1-20, an aryl group, or an alkyl radical, and X is chlorine, a bromine, or iodine.

R1-C6H4-SO2X (setting at each above-mentioned ceremony, R1 is a hydrogen atom or the alkyl group of carbon numbers 1-20, an aryl group, or an alkyl radical, and X is chlorine, a bromine, or iodine) etc. is mentioned.

[0043] The organic halogenide or halogenation sulfonyl compound which has functional groups other than the functional group which starts a polymerization as an initiator of an atomic migration radical polymerization can also be used. In such a case, the vinyl system polymer which has a functional group at one principal chain end, and has the growth end structure of an atomic migration radical polymerization at the principal chain end of another side is manufactured. As such a functional group, an alkenyl radical, a cross-linking silyl radical, hydroxyl, an epoxy group,

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2006/10/12

having a specific functional group from the degree of freedom of a design of an initiator or a catalyst being large, it is still more desirable. As this atomic migration radical polymerization method, Matyjaszewski et al. [for example,], Journal OBU American chemical society (J. Am.Chem.Soc.) 1995, 117 volumes, 5814 pages, macro leakage-at-bulb KYURUZU (Macromolecules) 1995, 28 volumes, 7901 pages, Science (Science) 1996, 272 volumes, 866 pages, WO 96/No. 30421 official report, WO 97/No. 18247 official report, WO 98/No. 01480 official report, WO 98/No. 40415 official report, or Sawamoto et al., 28 volumes, 1721 pages, JP.9-208818A, JP.8-41117A, etc. will be mentioned in macro leakage-at-bulb KYURUZU (Macromolecules) 1995.

[0032] In this invention, although which approach is used among these living radical polymerizations does not have especially constraint, an atomic migration radical polymerization method is desirable.

[0033] Although the living radical polymerization is explained below at the detail, the polymerization using 1 of the control radical polymerizations which can be used for manufacture of the vinyl system polymer later explained before that, and a chain transfer agent is explained. Especially as a radical polymerization using a chain transfer agent (telomer), although not limited, the following two approaches are illustrated as an approach of obtaining a vinyl system polymer with the end structure suitable for this invention.

[0034] They are the approach of obtaining the polymer of a halogen end, using halogenated hydrocarbon as shown in JP.4-132706A as a chain transfer agent, and a method of obtaining the polymer of a hydroxyl-group end, using a hydroxyl-group content mercaptan or a hydroxyl-group content polysulfide as shown in JP.61-271306A, JP.2594402B, and JP.54-47782A etc. as a chain transfer agent.

[0035] Below, a living radical polymerization is explained.

[0036] Among those, the approach using radical scavengers, such as a nitroxide compound, is explained first. Generally in this polymerization, a stable nit ROKISHI free radical (N-O·) is used as a radical capping agent. As such compounds, although definition is not carried out, the nit ROKISHI free radical from annular hydroxy amines, such as a 2, 2, 6, 6-tetramethyl-1-piperidinyloxy radical and a 2, 2, 5, 5-permutation-1-pyrroldinyl oxy-radical, is desirable. As a substituent, a with a carbon numbers [such as a methyl group and an ethyl group,] of four or less alkyl group is suitable. As a concrete nit ROKISHI free radical compound Although definition is not carried out, 2, 2, 6, 6-tetramethyl-1-piperidinyloxy radical (TEMPO), A 2, 2, 6, 6-tetraethyl-1-piperidinyloxy radical, A 2, 2, 6, 6-tetramethyl-4-oxo-1-piperidinyloxy radical, 2, 2, 5, 5-permutation-1-pyrroldinyl oxy-radical, 1, 1 and 3, and 3-tetramethyl-2-ISOINDORI nit oxy-radical, N, and N-G tert butylamine oxy-radical etc. is mentioned. Instead of a nit ROKISHI free radical, a free radical with a stable galvinoxyl (galvinoxyl) free radical etc. may be used.

[0037] The above-mentioned radical capping agent is used together with a radical generating agent. It is thought that the resultant of a radical capping agent and a radical generating agent serves as a polymerization initiator, and the polymerization of an addition polymerization nature monomer advances. Although especially both concomitant use rate is not limited, 0.1-10 mols of radical initiators are suitable to radical capping agent 1 Mol.

[0038] As a radical generating agent, although various compounds can be used, the peroxide which may generate a radical is desirable under polymerization temperature conditions. As this peroxide, although definition is not carried out, there are alkyls perester, such as peroxy carbonates, such as dialkyl peroxide, such as diacyl peroxide, such as benzoyl peroxide and lauroyl peroxide, ZIKUMIRU peroxide, and G t-butyl peroxide, diisopropyl peroxy dicarbonate, and bis(4-t-butyl cyclohexyl) peroxy dicarbonate, t-butyl peroxyoctoate, and t-butyl peroxybenzoate, etc. Especially benzoyl peroxide is desirable. Furthermore, radical generating agents, such as a radical generating nature azo compound like azobisisobutyronitril, can also be used instead of peroxide.

[0039] Macromolecules An alkoxy amine compound as shown in the following figure may be used as an initiator instead of using together a radical capping agent and a radical generating agent as reported by 1995, 28, and 2993.

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi_ejje

2006/10/12

JP.2003-113324.A [DETAILED DESCRIPTION]

8/10 ページ

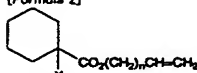
the amino group, an amide group, etc. are mentioned.

[0044] What has the structure which it is not limited as an organic halogenide which has an alkenyl radical, for example, is shown in a general formula (2) is illustrated. R4R5CO(X)-R6-R7-C(R3)=CH2 (2)

the inside of a formula, and R3 — hydrogen or a methyl group, and R4 and R5 — hydrogen — The univalent alkyl group of carbon numbers 1-20, an aryl group, an alkyl or the thing mutually connected in the other end, and R6 [or] — X in which (X) O- (ester group), -C(O)- (keto radical) or o-, m-, p-phenylene group, and R7 may include one or more ether linkage by direct coupling or the divalent organic radical of carbon numbers 1-20 is chlorine, a bromine, or iodine. As an example of substituents R4 and R5, hydrogen, a methyl group, an ethyl group, n-propyl group, an isopropyl group, butyl, a pentyl radical, a hexyl group, etc. are mentioned. R4 and R5 may be connected in the other end, and they may form the annular frame.

[0045] As an example of an organic halogenide of having the alkenyl radical shown by the general formula (1) XCH2C(O) O(CH2) nCH=CH2, H3CC(CH2) (H) (X) O(CH2) nCH=CH2, 2(H3C) C(X) C(O) O(CH2) nCH=CH2, CH3CH2C(H) (X) C(O) O(CH2) nCH=CH2, [0046]

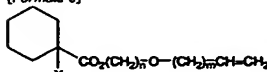
[Formula 2]



(Setting at each above-mentioned ceremony, for X, chlorine, a bromine or iodine, and n are the integer of 0-20)

XCH2C(O) O n(CH2) mCH=CH2, H3CC(CH2) (H) (X) C(O) O(CH2) nCH=CH2, 2(H3C) C(X) C(O) O(CH2) nCH=CH2, CH3CH2C(H) (X) C(O) O(CH2) nCH=CH2, [0047]

[Formula 3]



(Setting at each above-mentioned ceremony, for chlorine, a bromine or iodine, and n, the integer of 1-20 and m are [X] the integer of 0-20)

o, m, p-XCH2-C6H4-(CH2) n-CH=CH2, o and m, p-CH3C(H) (X)-C6H4-(CH2) n-CH=CH2, o and m, and p-CH3C — H2C(H) (X)-C6H4-(CH2) n-CH=CH2 (each above-mentioned formula — setting — X — chlorine —), A bromine or iodine, and n are the integer of 0-20.

o, m, p-XCH2-C6H4- n-O- (CH2) (CH2) m-CH=CH2, o and m, and p-CH — 3C(H) (X)-C6H4-(CH2) n-O-(CH2) m-CH=CH2, o and m, and p-CH3C H2 — C(H) (X)-C6H4-(CH2) n-O-(CH2) m-CH=CH2 (in each above-mentioned formula). For chlorine, a bromine or iodine, and n, the integer of 1-20 and m are [X] the integer of 0-20.

o, m, and p-XCH2-C6H4-O- (CH2) n-CH=CH2, o and m, and p-CH — 3C(H) (X)-C6H4-O-(CH2) n-CH=CH2, o and m, and p-CH3C H2 — C(H) (X)-C6H4-O-(CH2) n-CH=CH2 (each above-mentioned formula — setting — X — chlorine, a bromine, or iodine —), n is the integer of 0-20.

o, m, and p-XCH2-C6H4-O- n-O- (CH2) m-CH=CH2, o and m, p-CH3C (CH2) (H) — (X)-C6H4-O-(CH2) n-O-(CH2) m-CH=CH2, o and m, and p-CH3CH2C — (H) (X)-C6H4-O-(CH2) n-O-(CH2) m-CH=CH — two (in each above-mentioned formula) For chlorine, a bromine or iodine, and n, the integer of 1-20 and m are [X] the integer of 0-20.

The compound further shown by the general formula (3) as an organic halogenide which has an alkenyl radical is mentioned.

H2C=C(R3)-R7-C(R4)(X)-R8-R5 (3)

(the inside of a formula, and R3, R4, R5, R7 and X — the above — the same — R8 — direct

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2006/10/12

coupling, $-C(O)O-$ (ester group), and $-C(O)-$ (keto radical) or *o*-, *m*-, and *p*-phenylene group are expressed)

Although R8 is direct coupling or the divalent organic radical (one or more ether linkage may be included) of carbon numbers 1–20, when it is direct coupling, the vinyl group has combined with the carbon which has combined the halogen, and it is an allyl halide ghost. In this case, since carbon-halogen association is activated by the contiguity vinyl group, there may not necessarily be need of having C(O) O set, a phenylene group, etc. as R8, and may be direct coupling. When R7 is not direct coupling, in order to activate carbon-halogen association, as R8 O sets, a C(O) C(O) radical, and a phenylene group are desirable.

[illegible]

[0049] If the example of a halogenation sulfonyl compound of having an alkynyl radical is given, they will be *o*-, *m*-, *p*-CH₂=CH-(CH₂) *n*-C₆H₄-SO₂X, *o*-, *m*-, *p*-CH₂=CH-(CH₂) *n*-O-C₆H₄-SO₂X, etc. (setting at each above-mentioned ceremony, for X, chlorine, a bromine or iodine, and *n* is the integer of 0-20).

[0050] What has the structure which it is not limited especially as an organic halogenide which has the above-mentioned cross-linking silyl radical, for example, is shown in a general formula (4) is illustrated.

R4R5C(=O)-R8-R7-C(H)(X)CH2-C(S(R)9)2-C(Yb)0-Im-S(R10)3-C(Ya)4 (4)
the inside of a formula, and R2, R4, R5, R8, R7 and X — the above — the same — R9 and R10
All The alkyl group of carbon numbers 1-20, an aryl group, an aralkyl radical, or (R') 3SiO — (R') is
the univalent hydrocarbon group of carbon numbers 1-20 three (R') — being the same —
differing — ---- — when the Tori ORGANO siloxy radical shown is shown and R9 or two or
more R10 exist, they may be the same and may differ. When Yb is a hydrocarbon radical, Yb
shows 0, 1, 2, or 3, and b shows 0, 1, or 2, m is the integer of 0-19. However, k shall satisfy that
it is emb>=1.

If the compound of a general formula (3) is illustrated concretely XCH₂C(O) O nSi(CH₂)₃. CH₂C(OCH₃) (H) (X) C(O) O nSi(CH₂)₃, 2C(OCH₃) 2C(CH₃) (X) C(O) O nSi(CH₂)₃ C(OCH₃)₃. XCH₂C(O) O(CH₂) nSi(CH₃) (OCH₃)₃ 2C(CH₃) (X) C(O) O(CH₂) nSi(CH₃) (OCH₃)₃ 2C(CH₃) C(X) C(O) O(CH₂) nSi₂ (in each above-mentioned formula) (CH₃) (OCH₃). For X, chlorine, a bromine, iodine, and n are the integer of 0-20.

$\text{CH}_2\text{C}(\text{O}) \text{ n O}(\text{CH}_2) \text{ m Si}(\text{CH}_2) 3, \text{H}_3\text{CC}(\text{OCH}_3) (\text{H}) (\text{X}) \text{C}(\text{O}) \text{ n O}(\text{CH}_2) \text{ m Si}(\text{CH}_2) 3, (\text{OCH}_3) 2\text{C}(\text{H}_3\text{C}) (\text{X}) \text{C}(\text{O}) \text{ n O}(\text{CH}_2) \text{ m Si}(\text{CH}_2) 3, \text{CH}_3\text{CH}_2\text{C}(\text{OCH}_3) (\text{H}) (\text{X}) \text{C}(\text{O}) \text{ n O}(\text{CH}_2) \text{ m Si}(\text{CH}_2) 3, \text{CH}_2\text{CH}_2\text{C}(\text{OCH}_3) (\text{H}) \text{ n O}(\text{CH}_2) \text{ m Si}(\text{CH}_2) 3, \text{H}_3\text{CC}(\text{OCH}_3) (\text{H}) (\text{X}) \text{C}(\text{O}) \text{ n O}(\text{CH}_2) \text{ m Si}(\text{CH}_2) 3, 2, 2\text{H}_3\text{CC}(\text{C}(\text{X})(\text{O}) \text{C}(\text{H}_2) \text{C}(\text{O}) \text{CH}_2) \text{ m Si}(\text{CH}_2) 3, \text{OCH}_3) 2, \text{ and } \text{CH}_3\text{CH}_2\text{C}(\text{H}) (\text{X}) \text{C}(\text{O}) \text{CH}_2) \text{ n O}(\text{CH}_2) \text{ m Si}(\text{CH}_2) 3 (\text{CH}_3) 2$ (each above-mentioned formula — setting — $\text{X} = \text{chlorine}$ —) (OCH_3) . For a bromine, iodine, and n , the integer of 1–20 and m are the integer of 0–20.

[illegible]

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2008/10/12

(CH₂)₂-O-(CH₂)₃Si₃ (in each above-mentioned formula) (OCH₃). As for X, chlorine, a bromine, or iodine is mentioned.

[0051] As an organic halogenide which has the above-mentioned cross-linking silyl radical, what has the structure shown by the general formula (5) is illustrated further.

$$(R1O3-m)(Y)nSi[OSi(R9)2-b(Y)b]m-CH2-C(HX(R3))-R7-C(R4XX)-R8-R5 \quad (5)$$

(The inside of a formula, and R3, R4, R5, R7, R8, R9, R10, a, b, m, X and Y are the same as the above.)

[illegible]

(CH₃O) (CH₃) Si(CH₂/Si(CH₃)) (X-CO₂R, (CH₃O) Si(CH₃O) SO (CH₂) (R) (X-CO₂H,

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2006/10/12